Development of Novel Electrolytes for Use in High Energy Lithium-Ion Batteries with Wide Operating Temperature Range

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Project ID # es_37_srinivasan

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Start Date = April 2009
- End Date = April 2014
- Percent complete = 1%

Budget

- Total project funding
  - 875K total (~ 175K/year)
  - Contractor share = 0K
- Funding received in FY09
  - $175K

Barriers

- Barriers addressed
  - Enhance low temperature performance
  - Define performance limitations that limit life
  - Develop long life systems stable at high voltage

Partners

- Univ. Rhode Island (Brett Lucht)
  (Analysis of harvested electrodes, on-going collaborator)
- Argonne Nat. Lab (Khalil Amine)
  (Source of electrodes, on-going collaborator)
- Material Methods, LBNL (John Kerr)
  (Evaluation of novel salt, ex-situ analysis)
- A123 Systems, Inc.
  (Electrolyte development, on-going collaborator)
- Quallion, LCC.
  (Electrolyte development, on-going collaborator)
- Yardney Technical Products
  (Electrolyte development, on-going collaborator)
- Saft America, Inc.
  (Collaborator, industrial partner under NASA program)
- NREL (Smith/Pesaran)
  (Supporting NREL in model development by supplying data)

Objectives

- Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -30 to +60^{o}C).
- Improve the high temperature stability and lifetime characteristics of wide operating temperature electrolytes.
- Improve the high voltage stability of these candidate electrolytes systems to enable operation up to 5V with high specific energy cathode materials.
- Define the performance limitations at low and high temperature extremes, as well as, life limiting processes.
- Demonstrate the performance of advanced electrolytes in large capacity prototype cells.

Technical Approach

- **Electrolyte Development Approach:**
  - Optimization of carbonate solvent blends
  - Use of low viscosity, low melting ester-based co-solvents
  - Use of fluorinated esters and fluorinated carbonates as co-solvents
  - Use of novel "SEI promoting" and thermal stabilizing additives
  - Use of novel non-fluorine based salts (with Materials Methods, LBNL)
- **Electrolyte Characterization Approach:**
  - Ionic conductivity and cyclic voltammetry measurements
  - Performance characteristics in ~ 400 mAh three electrode cells
    - MCMB /$LiNi_{0.8}Co_{0.2}O_2$ cells, Graphite /$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cells
    - Use of high specific energy electrode materials (from in-house NASA program)
    - Electrochemical Impedance Spectroscopy (EIS) Measurements as function of temperature, high temperature storage, and cycle life
    - DC Tafel and linear (micro) polarization measurements on electrodes
    - Ex-situ analysis of harvested electrodes (URI and LBNL)
  - Performance characteristics in coin cells
    - Evaluation of electrolytes in conjunction with high voltage cathodes
- **Performance evaluation in prototype cells**
  - Yardney, A123, Saft, and/or Quallion Cells (0.300 mAh to 7 Ah size prototype cells)
  - Cells will be procured and/or obtained through on-going collaborations

Technical Summary

- The development of electrolytes that enable operation over wide temperature range, while still providing the desired life characteristics and resilience to high temperature (and voltage) remains a technical challenge.
- The current effort focuses upon the development of multi-component electrolyte formulations using various approaches including (a) solvent blend optimization, (b) use of novel co-solvents, (c) use of novel SEI and thermal stabilizing additives, and (d) the use of non-fluorine based salt.
- The electrochemical evaluation in proven three electrode test cell enables electrochemical characterization of each electrode (and interface) and the identification of performance limiting mechanisms. Electrodes are easily harvested from this test cell and samples will be delivered to collaborators (i.e., URI and LBNL).
- Performance testing of large capacity prototype cells containing candidate advanced electrolytes will be performed and evaluated under a number of conditions (i.e., assessment of wide operating temperature capability and life characteristics). JPL has on-going collaborations with a number of battery vendors and the capabilities to perform extensive testing.
- The program benefits from JPL's experience in the development and demonstration of advanced electrolytes for NASA applications, which have a similar need for long life, wide operating temperature systems.
- We welcome new collaborations !!

Inexpensive, Nonfluorinated Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

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05/21/2009

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Overview

Timeline

- Start: **April 2009**
- End: **March 2012**
- **0% complete**

Budget

- Total project funding
  $703,146
- Funding received in FY09
  $225K

Barriers

- Electrolyte **barriers** addressed:
  (i) identify **low-cost cell materials** and components
  (ii) **enhance abuse tolerance**
  (iii) **enhance low-temperature performance**

Partners

- **Richard Jow**, Army Research Laboratory (ARL), Adelphi, MD, USA
  electrolyte characterization/testing
- **Oleg Borodin**, University of Utah, UT, USA
  molecular modeling

Objectives

Develop **new anions** as **replacements for PF_6^- or** as **additives** for electrolytes:

- Anions produced from **inexpensive reagents** - potentially simpler than LiBOB to purify.
- Anions are **expected to form stable SEI layers** - possibly with lower impedance at low temperature than found with LiBOB. May also be **self-healing** and for the cyano-based anions may provide a polymerization **shut-off mechanism** during thermal abuse
- Other properties which salts based on these anions may exhibit include:

  (i) higher salt solubility in solvents (than LiBOB) to provide electrolytes with adequate Li^+ transport properties

  (ii) high thermal stability

  (iii) high cycling efficiency with low impedance at a wide range of temperatures

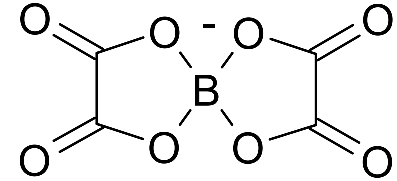
  (iv) low toxicity (organoborate-based anions)

  (vi) an electrochemical stability exceeding 4.3 V (vs. Li) (if SEI is suitable)

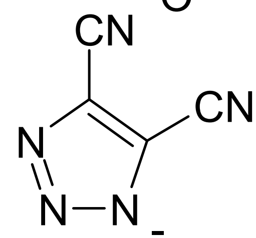
Approach

- Examine **two new classes of nonfluorinated anions** as potential replacements for PF_6^- to create new electrolyte formulations or additives to improve properties of current state-of-the-art electrolytes
- New anions based upon:

  (i) chelated and nonchelated **organoborate anions** (related to bis(oxalato)borate or BOB^-)



  (ii) Hückel-type anions in which the charge is stabilized on a **5-member azole ring** and noncyclic cyano-carbanions



- Salt **synthesis** and **purification** techniques will be optimized - the focus will be on lithium salts (LiX) and ionic liquids (combining the anions with organic cations)
- **Characterization** of solvent-LiX mixtures will include: thermal phase behavior/ phase diagrams, thermal stability, transport properties (viscosity, conductivity, diffusion coefficients, etc.), interfacial properties, electrochemical stability and corrosion properties with current collectors, degradation mechanisms, etc.
- **Cell performance testing**: charge/discharge performance (rates, low/high temperature, etc.), cycleability, abuse tolerance, use with alternative anodes and cathodes

Summary

- **New program beginning April 2009**
- Our approach is to **develop two classes of nonfluorinated anions** - this provides a greater probability of identifying salts which will meet the challenging goals of the program
- Collaborations - two **collaborations** have been identified thus far:
    - **Richard Jow** (Army Research Laboratory) will participate closely with the anion development and testing
    - **Oleg Borodin** (University of Utah) will assist with modeling of the electrolyte properties as data becomes available enabling a strong experimental-computational approach to be used

  Other collaborations will be established as necessary or desired to advance the project work towards achieving the program goals
- The postdoctoral fellow and graduate student at NC State University have already been identified and have begun work

Development of Electrolytes for Lithium Ion Batteries

Brett L. Lucht
University of Rhode Island

May 21, 2009

Project ID # es_37_srinivasan

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Overview

Timeline

- April 2009
- March 2014
- 0% complete

Budget

- Total project funding
  - DOE - $730K
- Funding received in FY09
  - DOE - $145K

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Rhode Island

Barriers

- Barriers addressed
  - Synthesize and evaluate novel electrolytes for lithium ion batteries
  - Improve cell performance, life and cost.

Partners

- M. Smart – NASA JPL
- Yardney technical Products/Lithion
- D. Abraham – ANL - ABRT

OBJECTIVES - DEVELOPMENT OF ELECTROLYTES FOR LITHIUM ION BATTERIES

- **Develop techniques to synthesize electrolytes that allow for lower cost of production.**

- **Develop low-cost, thermally stable electrolytes to replace ones now commonly used.**

- **Develop electrolyte/additive combinations that will facilitate a more stable solid-electrolyte interphase (SEI) on the anode.**

- **Develop additives that allow for the formation of protective coatings on the cathode (*i.e.*, a cathode SEI) and enhances electrochemical stability above 4.3 V.**

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Approach

- Investigate properties of $LiPF_4(C_2O_4)$/carbonate electrolytes in small (coin or pouch) lithium ion cells.
- Develop commercially viable low-cost synthetic method for production of $LiPF_4(C_2O_4)$ and Produce high purity $LiPF_4(C_2O_4)$ for LBNL or organizations designated by LBNL for additional testing.
- Develop Lewis basic thermal stabilizing additives for $LiPF_6$/carbonate electrolytes which prevent degradation of the anode SEI.
- Investigate combinations of thermal stabilizing additives and anode film forming additives in $LiPF_6$/carbonate electrolytes.
- Investigate cathode film forming additives which will allow the use of cathodes above 4.3 V.
- Investigate the surface of cycled cathodes and anodes with novel electrolytes or electrolyte/additive combinations to develop a mechanistic understanding of SEI formation and degradation.

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Summary

- Develop novel salts and additives for lithium-ion battery electrolytes.
- Preliminary results for $LiPF_4(C_2O_4)$, Lewis basic, and cathode film forming additives are promising.
- Use detailed electrochemical and surface analysis of electrodes to understand effect of electrolyte modification.
- Collaborations with Yardney/Lithion, M. Smart NASA-JPL, D. Abraham ANL-ABR.
- Results will be published in peer reviewed literature and presented at technical meetings.
- Post-Doc, graduate and undergraduate student training.

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